54-9.24

NACA

RESEARCH MEMORANDUM

PRELIMINARY INVESTIGATION OF THE "FREEZE-CASTING" METHOD FOR FORMING REFRACTORY POWDERS

By W. A Maxwell, R. S. Gurnick, and A. C. Francisco

Lewis Flight Propulsion Laboratory
Cleveland, Ohio

NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS
WASHINGTON
March 9, 1954

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

RESEARCH MEMORANDUM

PRELIMINARY INVESTIGATION OF THE "FREEZE-CASTING" METHOD FOR FORMING REFRACTORY POWDERS

By W. A. Maxwell, R. S. Gurnick, and A. C. Francisco

2855

CC-1

SUMMARY

A method of preparing intricately shaped objects such as turbo-supercharger blades from refractory powders was investigated. The method consists in preparing an extremely thick slip of such materials as titanium carbide with a small amount of binder, casting the slip into a mold, and freezing to retain the shape of the casting. The casting is then dried by sublimation and may subsequently be sintered by conventional means.

It was found possible to cast high-solid-content slips by employing vibration during the casting process. Turbosupercharger blades of good appearance and free from radiographic flaws were produced. The production of sound bodies depends on a dry casting of high density. Factors affecting the density of a casting before sintering are a high ratio of powder to liquid in the casting slip, maximum particle size of the powder, deaeration of the slip, and the use of vibration to increase the flow of the high-solid-content slip.

INTRODUCTION

Many of the refractory carbides, oxides, silicides, and cermets possess outstanding strength and oxidation resistance at high temperatures and are promising for turbine-blade use. In addition, a large number of them are prepared from noncritical materials.

The application of cermets and ceramics to turbine components where physical properties permit is predicated on high rates of production at reasonable cost. Conventional metallurgical casting techniques cannot be used because of the elevated melting points and the lack of suitable mold materials.

Because of the uniform high hardness and room-temperature brittleness of the materials, present methods of forming consist essentially

in grinding either fully or semisintered blanks to shape. Despite the recent developments of arc machining and similar techniques (ref. 1), machining of the complex turbine-blade airfoil from a fully sintered and fully hard blank does not appear attractive. Machining or grinding of pressed or semisintered blanks is more easily accomplished. During the subsequent sintering, the blank is subject to possible distortion, cracking, and shrinkage.

A survey of the literature indicates that at present there is no satisfactory method for the production of fully formed turbine blades directly by cold- or hot-pressing. Slip casting offers a method for the production of fully formed blades without the subsequent removal of appreciable amounts of material. The slip-casting process consists briefly in preparing a slip or suspension of the powder in water. The slip is then poured into an absorbent plaster-of-paris mold.

2855

As the water is absorbed into the mold, the solid particles build up on the mold surface. The amount of solids deposited depends on the time permitted for absorption; and for objects such as turbine blades, the mold would be kept completely filled until a solid casting results. An important disadvantage of the process is that the particle sizes necessary for optimum casting, or sintering, properties may not be the same. Other disadvantages are that the powders may segregate during casting or absorption, especially in solid castings, and that low "green" densities with resulting high shrinkages and danger of distortion are frequently obtained. While such oxides as beryllia and alumina have been successfully cast and cermet combinations have been cast on an experimental basis, there appears to be no commercial slip casting of metallic materials; and the applicability of the conventional slip-casting techniques to all the materials of interest has not been demonstrated.

It appeared that the slip-casting process might be modified so as to apply to a wider range of materials and particle sizes. To do this it seemed essential to remove the necessity of forming a suspension of the powder. The liquid used would then provide only fluidity and if the quantity of liquid could be sufficiently reduced, absorption into the mold would not be essential. To retain the shape of the cast object so as to permit its removal from the mold, it would be necessary to have the liquid set or contain a setting binder. Another alternative was to freeze the casting and to remove the object while the liquid was in the solid state. The frozen liquid would then serve as a temporary binder with another conventional binder included in the slip to retain the shape of the dried casting.

Freezing a fluid slip in a mold appeared feasible but several other problems remained. The investigation of these problems comprise the basis of this investigation. The most important problems are:

(1) Casting a slip with little or no fluidity

(2) Elimination of distortion and cracking while drying

(3) Removal of the frozen castings from the mold

(4) Selection of a suitable binder

In view of the large number of variables involved and the modifications of techniques possible, the investigation as conducted at the NACA Lewis laboratory was limited to these problems and to determining the general feasibility of the method for producing sound specimens, using radiographic examination as the criterion.

The types of casting investigated were:

(1) Single component, completely sintered turbosupercharger blades, using molybdenum disilicide and molybdenum metal to represent this type of material

(2) Partially sintered titanium carbide blades for subsequent infiltration with metal to prepare a cermet body

(3) Composite blades of aluminum oxide and metal to investigate the possibility of preparing a blade with a ductile alloy root and a ceramic blade

PROCEDURE AND COMMENTS

Freeze-Casting Method

The freeze-casting method as developed is shown on flowsheet form in figure 1 and the processes are discussed in order as shown. The powders employed with their particle sizes are listed in table I.

Mixing of slip. - A water solution of starch was added to the powder from a burette in quantities as shown in table II. This solution was prepared to contain an amount of starch binder equal to 2 percent of the weight of the powder in the volume added. After the powder had absorbed the liquid, further mixing was done by holding the container on a vibrator and manipulating with a spatula. The vibrator was of constant frequency (60 cycles) and a variable amplitude. The power input and related amplitude could be adjusted to give rapid mixing. Vibration is essential during the mixing operation because the low fluid content does not permit the flow of particles past each other as in ordinary mechanical mixing. All the slips would stand without slumping and only a few of the more fluid could be hand worked without crumbling.

The requirements of a binder for this process are that it impart sufficient green strength to the casting, dry well in vacuum, and not unduly increase the viscosity of the fluid. Starch was selected after trial of such conventional materials as gum arabic, gum tragacanth, glue, gelatin, and methylcellulose.

Deaeration. - Removal of entrapped air in the slip was accomplished in the apparatus shown schematically in figure 1(b). An amount of slip sufficient for the casting of a specimen was mixed and placed in the injector. With the plunger locked, a tube with rubber seal was placed over the inverted injector and a vacuum of 26 inches of mercury rapidly drawn while vibrating. After subsidence of the air bubbles, the vacuum was quickly released to prevent undue evaporation. Treatment of the slip in the injector used for casting minimizes the entrainment of air in handling which might occur if separate vessels were used. Unlike commercial deaeration equipment, however, there was no mechanical working of the slip. 2855

Casting. - After deaeration, the injector was clamped to the mold, the plunger lock released, and the assembly placed on the vibrator as shown in figure 1(c). The weight of the mold was sufficient to force the slip into the mold under vibration. Mold filling was determined by ejection of the slip from the risers.

The molds used in the investigation are shown in figure 2. Blade d (fig. 3, mold 1) was patterned on alloy turbosupercharger blades, while blade f (mold 2) embodied modifications for a cermet blade. Molds were prepared from the low-melting lead-bismuth alloy Cerrotrue as it could be readily cast about a wooden pattern. While these molds were inexpensive and quickly prepared, they are not sufficiently abrasion resistant and must be chromium plated for increased mold life. The optimum mold material should have a hard surface, good thermal conductivity, and sufficient strength to withstand freezing pressures.

Freezing. - After detaching the injector, the filled molds were placed in a bath of Varsol (a petroleum fraction) and solid carbon dioxide (dry ice). Freezing times were from 5 to 10 minutes at -40° F. The freezing rate was controlled by heat-transfer rate through the relatively heavy molds. No detailed survey of the effects of bath temperatures was made.

Casting removal. - Removal of castings from the molds has caused the greatest difficulty of any step in the process. The expansion of water on freezing, as in the case of type-metal, has the beneficial effect that the solidifying casting is forced to follow the outline of the mold. However, this expansion does not simplify removal of the casting. It was found that a thin coating of talc on the chromium-plated surface of the mold resulted in reasonably satisfactory casting removal if considerable care was exercised.

2855

Drying. - On removal, the frozen castings were placed immediately in a vacuum chamber and held at a 1 to 5 microns pressure for 2 hours. While sublimation produces some cooling, it is still necessary to support the casting on an insulator to block out conducted heat and to prevent melting. No difficulty was encountered in drying turbosupercharger blades without distortion if the castings were placed on a pad of cotton batting. The light weight of the turbosupercharger blade probably minimizes distortion.

Sintering. - While the freeze-casting process is properly concerned only with the production of shaped, unsintered objects, subsequent steps may be of interest.

The furnace used is shown in figure 4. The vacuum is produced by a conventional system and heating is by resistance. A tungsten coil was used as the resistance element in an enclosed cylinder about the crucible as shown diagramatically in figure 1(g). Power input to the coil was from a motor-driven variable transformer. As the speed of the motor driving the transformer control was adjustable over a wide range, sintering and cooling cycles could be easily changed. Temperatures were read and recorded from a thermocouple inserted almost to the center of the crucible.

The only difference to be expected in sintering a freeze-cast object in its final form as compared with a cold-pressed bar is that more precautions are necessary to prevent distortion. Packing the blades in -325 mesh alumina held in a porous alumina crucible with a sealed top and thermocouple well was found to keep distortion within allowable limits without loss of powder to the vacuum system.

Infiltration. - Semisintered titanium carbide blades were infiltrated by the method described in reference 2. Briefly, this consists in placing the blade vertically in a mold surrounded by a susceptor in an induction furnace with a piece of the infiltrant of the desired weight placed on top of the blade. The temperature is then raised until the metal becomes fluid and is absorbed into the porous blade by capillary action.

Evaluations

Densities. - The densities of fully sintered blades were determined by the conventional water-immersion method. For the green, as-cast blades, the high porosity and intricate shape made determinations of volumes difficult. An indirect method was therefore employed. For this method, blades of dental plastic of known density and negligible shrinkage were cast in the freeze-casting molds. The volume of the

mold cavity could then be determined by the water-immersion method. As the shrinkage of the powder blades was greater than that of the plastic, the densities of the freeze-cast blades could only be approximated using this volume. However, the accuracy was sufficient for comparison purposes.

Soundness. - Radiographs taken by conventional means were used as a criterion of soundness. In most cases both high- and low-density exposures were made to improve sensitivity.

2855

Effect of vibration frequency on flow of slip. - To determine the frequency at which the slips employed flowed most rapidly, the apparatus sketched in figure 5 was employed. This apparatus consists of a flat plate with a holder positioned as shown. A 1- by 1- by 1-inch cavity was centered over the plate and lines were scribed in front of it at 1-inch intervals. The plate was mounted on a loud speaker which was driven by a beat frequency oscillator. The cavity was filled with slip and trowelled flat to give 1 cubic inch of sample. Measurements could then be made of the time required for the slip to slump and flow out over a selected line at various frequencies. The amplitude, however, was not controlled.

RESULTS AND DISCUSSION

Applicability of Method

Blades cast from titanium carbide, aluminum oxide, molybdenum metal, and molybdenum disilicide powder are shown in figure 3. Data for these materials are given in table II. A composite blade having an airfoil section of titanium carbide and a root of aluminum oxide is shown in figure 6. The constituents were mixed separately and charged into the injector in the proper quantities and order. Mixing of the constituents took place only in a narrow zone joining the two. All the material tried cast in a satisfactory manner and there appears to be no important difference in quality of the castings for such diverse materials as the metal molybdenum and aluminum oxide. It must be emphasized that the process is one in which technique is of considerable importance, and minor differences in the castability of materials may not have been revealed because of the operator's inexperience.

Molybdenum disilicide was used for most of the investigation of single-component fully sintered blades because of its convenient sintering temperature and high-temperature strength (ref. 3). The radiograph of a sound blade is shown in figure 7. In this case the effects of particle size and powder-to-liquid ratio in the slip on the properties of the castings were studied. Some of the properties of the cast material are given in table II.

A titanium carbide blade infiltrated with Inconel is shown in figure 8(c) with a radiograph (fig. 8(b)) and a radiograph of the original casting (fig. 8(a)). The behavior of the semisintered freeze-cast titanium carbide blade during infiltration was similar to that of blanks produced by machining semisintered cold-pressed blocks of titanium carbide (ref. 2). In respect to surfaces and radiographic flaws, the freeze-cast blade compares well with those produced from cold-pressed blocks. The microstructure as shown on figure 9 is clean and free from voids. The freeze-casting method would appear to offer a convenient method of preparing preformed blanks for the infiltration technique and for the production of small intricately shaped parts where the shape is the important consideration.

Factors Affecting Soundness

Unsoundness in castings made by freeze casting appears to be due to air holes, or bubbles, and cracks attributed to shrinkage in drying or sintering. On the basis of radiographs, segregation does not appear to be a problem although this might become apparent in larger castings. The presence of air holes may be attributed to inadequate deaeration, or to entrainment of air during injection. It was indicated that, except for extremely thick slips, the difficulty may be eliminated by careful deaeration and injection under vacuum. The problem of crack prevention appears more difficult, and the solution would appear to lie in reducing drying shrinkage, as in conventional ceramics (ref. 4). The ratio of the powder to liquid by weight in the slip can be computed from the component weights listed in table II. It was observed that lower solid-to-liquid ratios tended to give sounder castings as shown by the radiographs. However, when the fluid content of the slip was reduced too drastically, the slip, although castable, could not be completely deaerated and air holes were found in the castings.

Another factor which has a marked effect on the optimum powder-to-liquid ratio and the related cast density is the powder particle size. As shown in table II, increases in particle size for molybdenum disilicide made it possible to decrease the amount of fluid in the slip and resulted in higher slip densities. The fact that less fluid is required for equal flow characteristics in a coarse powder may be attributed to the lower specific surface area. As less surface is present, less fluid is required to wet it. Although densities can be improved by increases in particle size, the maximum that can be employed will be limited by sintering conditions. If powders that are too coarse are employed, sintering times and temperatures may become excessive.

A study of the effect of vibration frequency on the flow characteristics of a typical titanium carbide slip made on a loudspeaker setup

(fig. 5) showed that flow was most rapid at frequencies between 35 and 40 cycles per second. At 60 cycles per second, the flow was only two-thirds as rapid. The effect of vibration quickly decreased with further increase in vibrational frequency, and at 80 cycles and above, no flow of the slip was observed to 30,000 cycles per second, the maximum investigated. The casting vibrator operated at 60 cycles per second.

SUMMARY OF RESULTS

2855

A method of preparing intricately shaped objects from refractory powders was investigated.

1. The basic steps in the procedure are:

(a) Preparation of an extremely thick slip of the powder in a fluid containing a binder

(b) Casting of the slip into a mold

(c) Freezing of the slip to retain the shape of the mold

(d) Removal of the liquid by sublimation drying

(e) Sintering of the dried casting

2. A high-density dry casting is desirable for sound sintered bodies. This depends on a combination of the following points to achieve the desired results:

(a) A high ratio of powder to fluid to reduce drying and sintering shrinkage

(b) Maximum particle size of the powder compatible with practical sintering conditions

(c) Deaeration of the slip

(d) The use of vibration to move the high-solid-content slips in casting

Turbosupercharger buckets of good appearance and free of flaws detectable by radiography were produced in both full-sintered and semi-sintered conditions.

Lewis Flight Propulsion Laboratory
National Advisory Committe for Aeronautics
Cleveland, Ohio, December 8, 1953

2855

REFERENCES

1. Minerals and Metals Advisory Board of National Research Council: Conserve Diamond Bort and Cut Hard-to-Machine Materials with New Machining Processes. Jour. Metals, vol. 4, no. 4, Apr. 1952, pp. 378-380.

2. Gurnick, Raymond S., and Cooper, Anthony L.: Infiltration of Titanium Carbide with Several Metals. NACA RM E52E27, 1952.

3. Maxwell, W. A.: Some Stress-Rupture and Creep Properties of Molybdenum Disilicide in the Range 1600° to 2000° F. NACA RM E52D09, 1952.

4. Norton, F. H.: Elements of Ceramics. Addison-Wesley Press, Cambridge (Mass.), 1952, p. 111.

CC-2

TABLE I. - POWDER USED IN FREEZE-CASTING INVESTIGATION

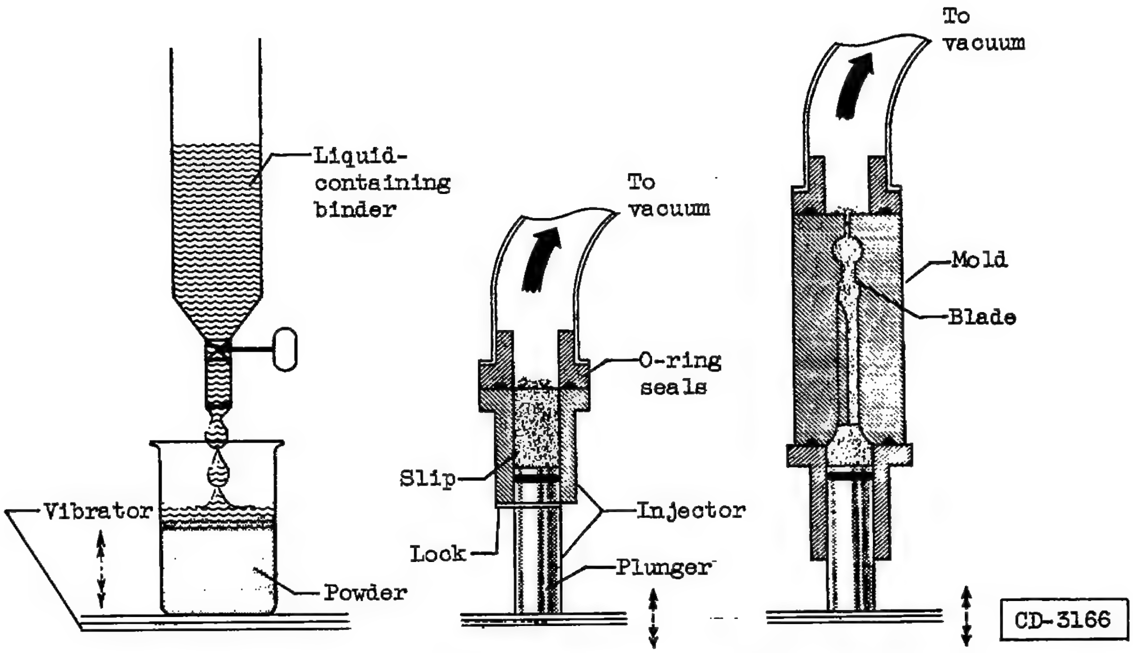
Powder	Sources	Particle size, percent
$MoSi_2$, "Small particle size"	NACA	100 Minus 6 microns 98 Minus 1 micron
$MoSi_2$, "Large particle size"	NACA	1 Larger than 15 microns 1 Smaller than 15 microns, larger than 11 microns 3 Smaller than 11 microns, larger than 7 microns 11 Smaller than 7 microns, larger than 3 microns 33 Smaller than 3 microns, larger than 1 micron 51 Smaller than 1 micron
Titanium carbide	Kennametal, Inc.	10.4 Smaller than 11 microns, greater than 7 microns 58.2 Smaller than 7 microns, greater than 3 microns 29.2 Smaller than 3 microns, greater than 1 micron 2.9 Smaller than 1 micron
Molybdenum metal	Charles Hardy Co.	4 Microns average particle size
Aluminum oxide	Norton Co.	100 Minus 325 mesh

TABLE II. - DATA FOR REPRESENTATIVE FREEZE CASTINGS

Powder particle size (a)	Slip		Powder-to-liquid ratio	Density		Radio-graph	Appearance
	Powder, g	Liquid, ml		Dried casting	Sintered		
Molybdenum disilicide							
Small -1	20	6.2	3.22	----	----	Poor	Good
Small -1	25	8.25	3.03	----	----	----	Good
Large -2	25	4.7	5.31	2.76	----	Poor	---------
Large -2	30	3.8	7.89	2.92	5.84	----	Air holes
Large -2	30	5.8	5.17	----	5.58	Good	Good
Large -2	30	5.8	5.17	2.88	5.65	Good	Good
Aluminum oxide							
5	20	5.9	3.38	----	----	Good	Good
Molybdenum metal							
4	25	6.2	4.03	----	----	----	Good
Titanium carbide for infiltration							
3	30	6.25	4.80	2.44	----	Poor	Good
3	30	5.65	5.30	2.54	----	Good	Air hole
3	30	5.70	5.20	2.59	----	Good	Good
Composite blade alumina root, molybdenum disilicide							
5	10	4.2	----	----	----	----	---------
1	20	2.4	----	----	----	----	---------

[a]Numbers refer to particle size data on table I.

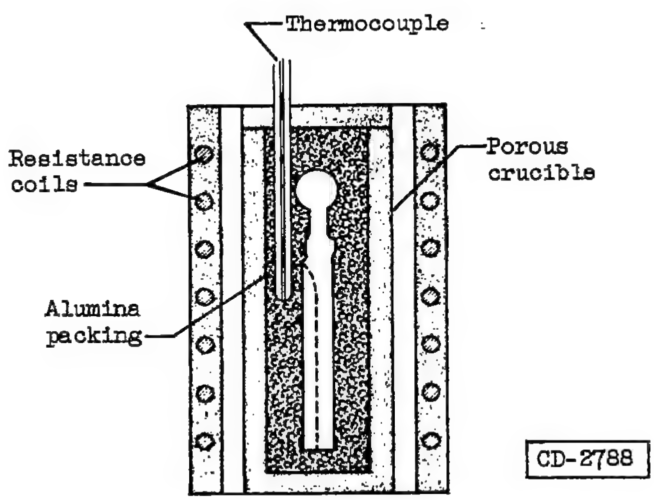
2855



(a) Mixing.

(b) Deaeration.

(c) Injection or casting.



(g) Sintering (or presintering for infiltration).

Figure 1. - Steps in freeze-cast method. Steps (d), freezing; (e), casting removal; and (f), drying are not shown.

C-27973

(a) Mold 1. (b) Mold 2.

Figure 2. - Chromium-plated Cerrotrue dies as used for freeze-casting experiments. Castings were made with root section up.

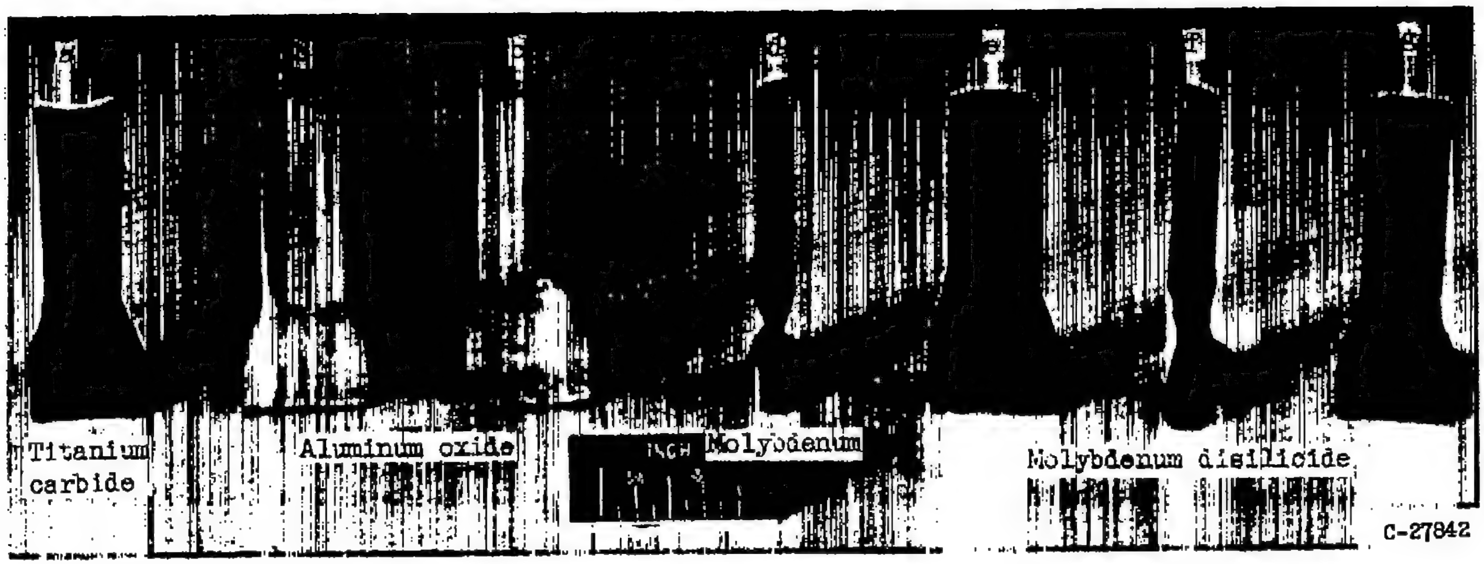


Figure 3. - Freeze-cast turbosupercharger blades as cast.

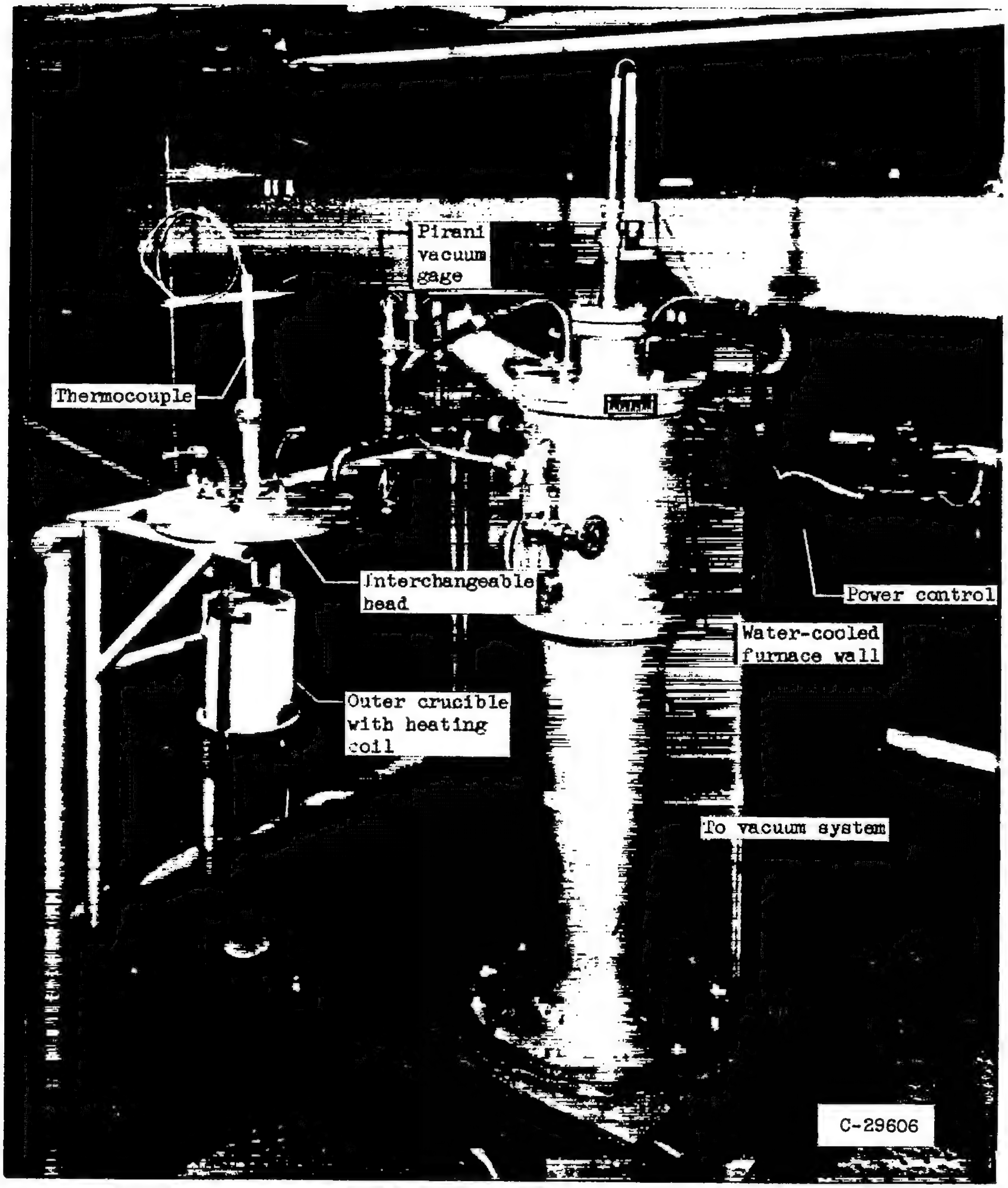


Figure 4. - Vacuum furnace and automatic control. Extra furnace head at left.

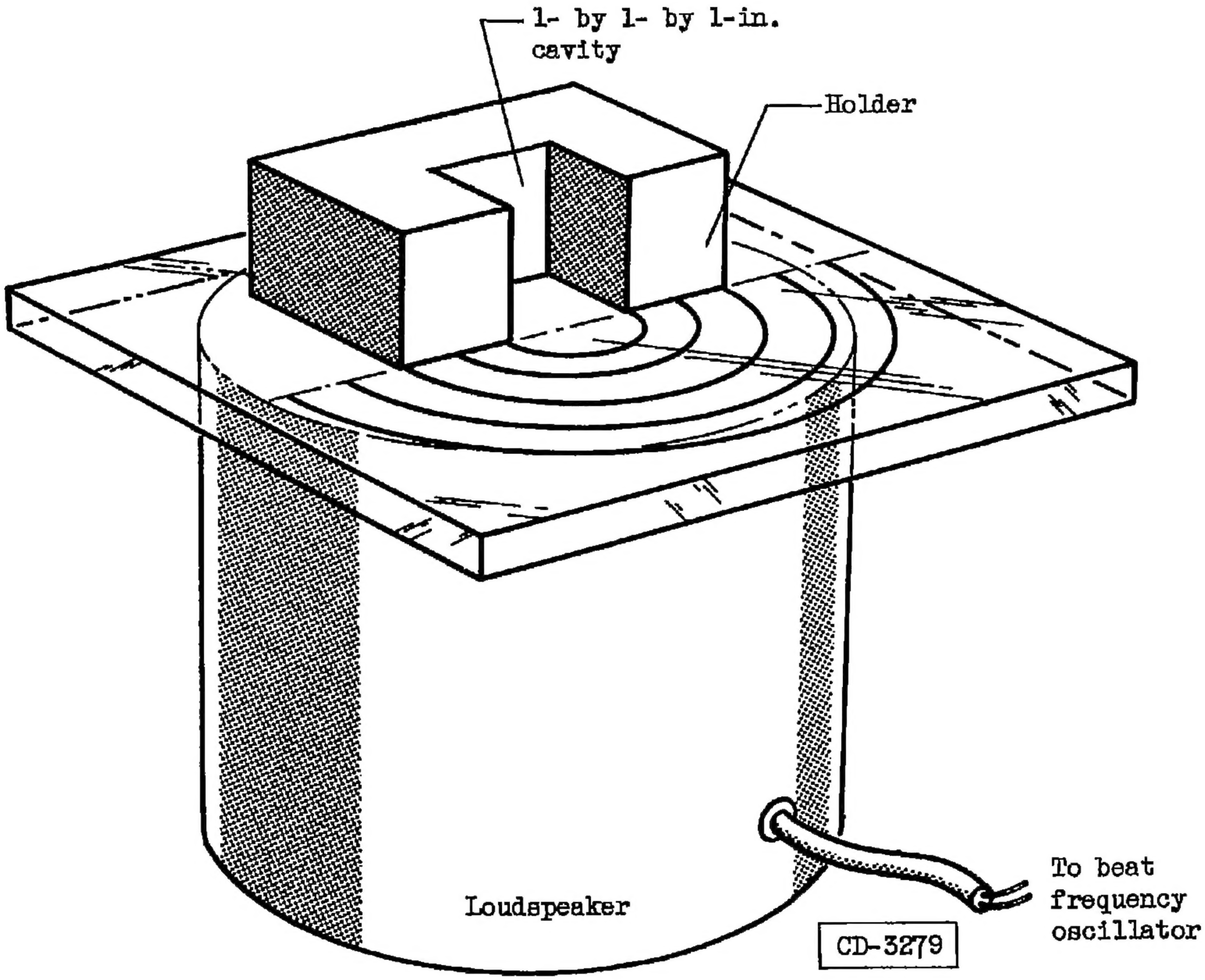
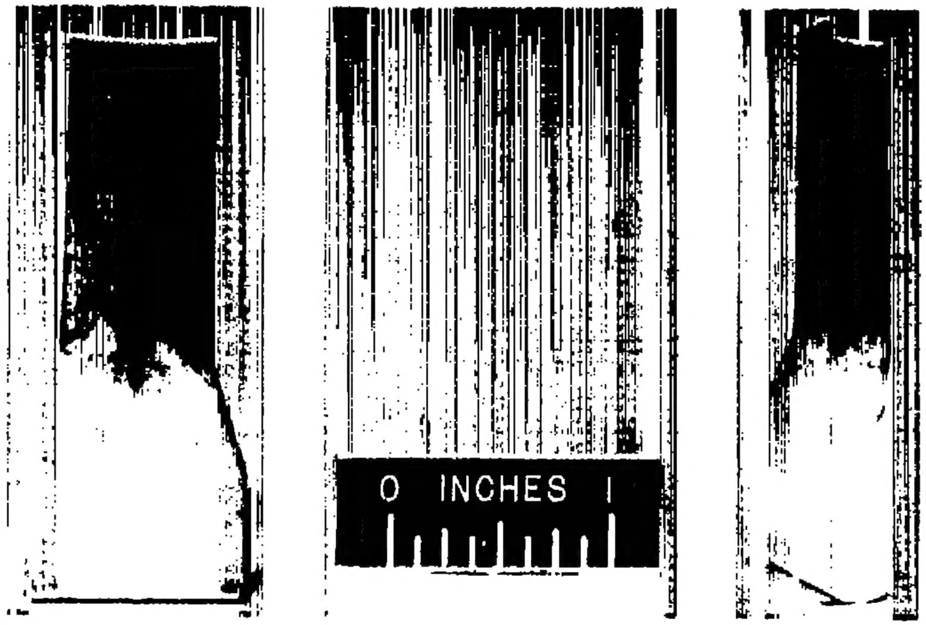


Figure 5. - Plate and cavity arrangement used for measuring the effect of vibratory frequency on speed of flow of thick slips.



C-27982

Figure 6. - Composite freeze-cast turbosupercharger blade in as-cast condition. Titanium carbide blade, alumina root.

C-34414

Figure 7. - Radiograph of molybdenum disilicide sintered blade.

C-34415

(a) Radiograph of blade after presintering for 2 hours at 2300° F.

(b) Radiograph after infiltrating with Inconel.

(c) Photograph of finished blade.

Figure 8. - Infiltrated titanium carbide plus Inconel blade at various stages in preparation.

2855

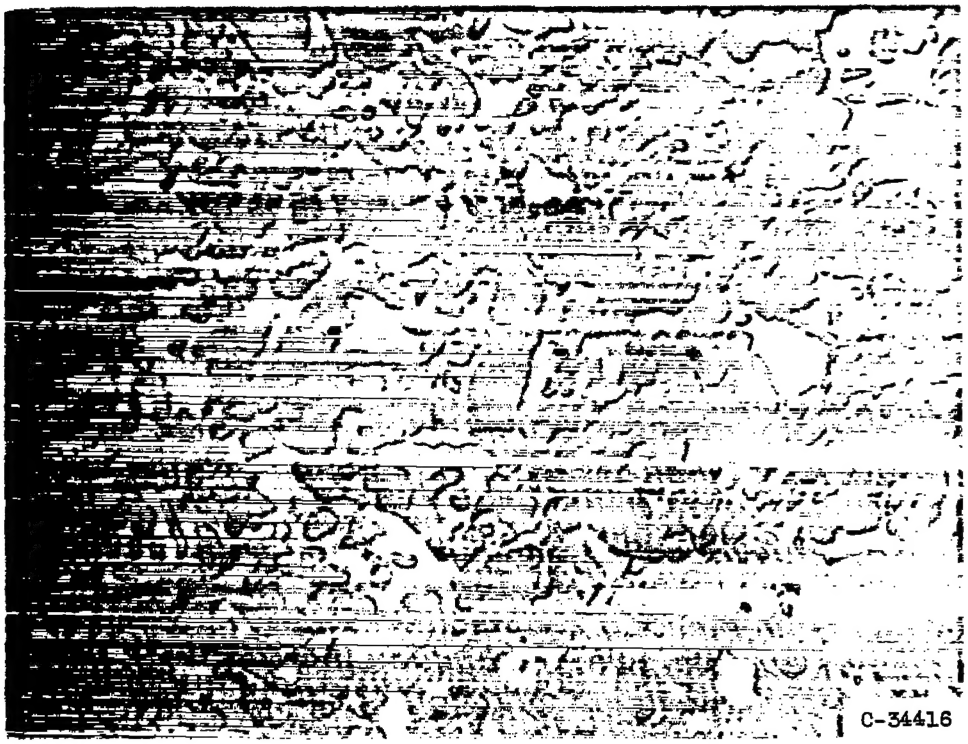

C-34416

Figure 9. - Photomicrograph of freeze-cast titanium carbide infiltrated with Inconel. X1000